Senior Thesis

An Integrated Approach to Recognizing Fossil Cold Seeps: Methodology and Application

By

Brad Cramer

2002

Submitted as partial fulfillment of
the requirements for the degree of
Bachelor of Science in Geological Sciences
at The Ohio State University
Spring 2002

Approved by:

Dr. Mathew R. Saltzman

An integrated approach to recognizing fossil cold seeps: Methodology and Application

Bradley D. Cramer*

Department of Geological Sciences, The Ohio State University, Columbus, Ohio 43210

*E-mail: cramer.70@osu.edu

ABSTRACT

Methane has become an attractive answer for the anomalous and has recently been used to explain numerous carbonates, especially mud mounds, in the rock record. The criteria for recognizing methane seeping from the sea floor (cold seeps) have not been standardized, resulting in a variety of arguments asserting the influence of methane. This study is an attempt to classify six criteria which would allow for the positive identification of a fossil cold seep; independent of age, geologic setting, depositional depth, or lithology.

Keywords: methane, cold seeps, carbonate mud mounds, anaerobic methane oxidation, sulfate reduction, carbon isotopes, methanogenesis, syntrophic

Introduction

The study of methane has grown considerably in the past two decades, especially in light of recent estimates of the amount of carbon tied up in the total methane pool (e.g. Kennedy et al. 2001). The discovery of chemosynthetic communities off the Galapagos

Islands in 1977 (Corliss et al. 1979; Ballard 1977) has lead to further research involving methane, and recent advances in microbiology have given us the culprits responsible for the foundation of life in these strange environments (e.g. Orphan et al. 2001). Methane has become a solution often turned to for explaining the anomalous, and is a favorite explanation for carbonates found in areas where carbonate production seems unlikely. This study attempts to provide a diagnostic test against which suspected methane seeps (cold seeps) can be investigated.

One of the first predictive tests for the identification of fossil cold seeps was created by Campbell (1992). This study is an attempt to further that work, and incorporate the advances made in the biochemistry of chemosynthesis in the past decade. The Campbell (1992) model for recognition of fossil cold seeps particularly from convergent margin settings runs as follows. One should expect to find:

- Offshore marine strata with anomalous carbonates and sulfides as well as a light stable carbon record.
- Unique faunal assemblage (high abundance, low diversity).
- Preserved structural conduit for fluid flow.

In order for a paleoseep site to be recognized, we must begin with several initial presumptions. There must be a source of the methane, a pathway for it to move, it must then move, and there will be consequent effects of this; namely biologic, geochemical, and physiographic.

There must be a source. My initial wording on this was to be `underlain by an organic rich unit`, however there are instances where a stratigraphic relationship is not the case. Paull et al. (1992) report a modern methane seep from the base of the Florida

Escarpment, at the very distal edge of the Mississippi Delta. Ground water recharge from high up the delta enters the delta complex, where it picks up extremely light biogenic methane eventually being expelled via density driven down slope movement at the escarpment, creating cold seep communities. This shows a non-stratigraphic relationship between the organic rich source and the seep.

There must be a pathway. This should be some physical conduit allowing the methane more freedom of movement than simply porosity. If typical ocean sediment porosity alone was enough of a conduit to allow for methane seepage to produce a chemosynthetic community, shouldn't we expect to find seeps absolutely everywhere there are organic rich, methane bearing units beneath the sea floor? It is a structural feature that most often provides this pathway or conduit (fig. 2a).

Assuming the above arguments are fulfilled, the methane must move if it is to create a seep. We should then expect to find a record (see Hovland 1992 for a review).

Finally, if all three above cases are true, there will be consequences we should be able to find in the rock record. Biologic: The presence of hydrocarbons seeping from the sea floor provides a novel nutrient source. We expect to find a faunal assemblage unique from and inconsistent with the surrounding benthic community, due to the localized, anomalous energy source utilized by the seep community. Geochemical: The isotopically depleted methane should leave behind evidence of its presence, since anomalous carbonates are common in modern cold seeps, and they record this anomalously light carbon source (e.g. Sassen et al. 1998). Finally the presence of fluid expulsion at the seep should leave behind some physiographic record of its movement.

These are the basic arguments the following diagnostic test is attempting to satisfy. The test does not follow the above pathway (from source to effect), and is instead presented in "field format"; the steps from initial consideration of worth looking into, to further field investigation, to final laboratory analysis. The proposed diagnostic test for recognition of fossil cold seeps follows.

Carbonate Deposition in an Otherwise Siliciclastic Setting

Anaerobic methane oxidation coupled with sulfate reduction,

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^- + HS^- + H_2O$$

provides bicarbonate and increases alkalinity, thus is the primary driver in precipitation of carbonates at seep sites (e.g. Paull et al. 1992; Aharon and Fu 2000). This metabolic pathway is the dominant consumption pathway of methane in marine sediments (Pancost et al. 2001; Hinrichs et al. 2000), and allows for carbonate precipitation in settings dominated by siliciclastics where carbonate production would be unlikely.

Presence of One or More Physiographic Feature

Carbonate crusts of a circular or dome shape are common at modern cold seeps (Orange et al. 1999; Hovland 1992; Corselli and Basso 1996). The style and intensity of fluid movement can be inferred from the morphology of the carbonates. For example, diffuse fluid movement can result in slabs, nodular carbonates, or tiny bubble tubes while concentrated movement often results in chimneys, carbonate mounds, or mud volcanoes (Orange et al 1999, Wiedicke et al. 2001; von Rad et al. 1996; Campbell and Bottjer 1993, Kulm and Suess, 1990). Some common features of cold seeps include: mud volcanoes, chimneys, carbonate "doughnuts", carbonate mounds, anomalous fans (Paull et al. 1992), mud diapirs (Orange et al 1999), pockmarks (von Rad et al. 1996), mushroom shaped structures and disc shaped rocks (Hovland 1992), bioherms and bacterial mats (Sassen et al. 1998). This list is not all inclusive and like the other test criteria, as long as each test is sufficiently fulfilled, the test can continue.

High Abundance Low Diversity Fossil Assemblage

The high abundance low diversity nature of the anomalous faunal assemblages that make up a seep community are useful indicators for identifying a fossil cold seep. Seep communities use an altogether different energy source than the usual denizens of the deep with H_2S and CH_4 as the foundation of the food chain (c.f. Campbell and Bottjer 1995; Corselli and Basso 1996). Microbes living inside higher faunal tissue, act to symbiotically provide an energy source for the higher organism by oxidizing the carbon and reduced sulfur from methane and hydrogen sulfide respectively (e.g. Cary et al. 1988; Campbell 1992; Cavanaugh et al. 1987). This unique energy source leads to a faunal assemblage dissimilar to the typical marine community. Since the specialization requirement is so high, i.e. an entirely different energy source, the odds of "outsider" colonization are slight (Tunnicliffe 1992). This restricted access to an ample energy source leads to the high abundance low diversity population.

Rio et al. (1992) showed, albeit with only limited samples, a divergence in carbon isotopic data between organisms living with symbiotic zooxanthellae and those living with chemosymbiotic bacteria. Those with zooxanthellae show a $\delta^{13}C$ decrease during skeletal growth while those with chemo-endosymbionts show a $\delta^{13}C$ increase during skeletal growth; those organisms without symbionts show no appreciable trend (all $\delta^{13}C$ values reported herein are relative to the PDB standard). Perhaps this could be further used to help identify those organisms capable of living in a seep setting in the distant rock record.

There is a considerably larger volume of literature on those organisms living in hydrothermal communities than those living at cold seeps, however many researchers have referred to biology occurring in both settings simultaneously. Rio et al. (1992) and particularly Tunnicliffe (1992) give an extensive list of the typical organisms from modern hydrothermal vent/cold seep communities. Somewhere on the order of 90% of the species found at hydrothermal vents/cold seeps are found nowhere else on earth. In the hydrothermal vents and to some extent cold seeps as well, it is the vestimentiferans (tube worms) that dominate the landscape accounting for a fair majority of the biomass (Tunnicliffe 1992; Orange et al. 1999; Paull et al. 1992; MacAvoy et al. 2002). However the unlikely preservation of tube worms leaves something to be desired as a fossil indicator.

I have purposefully refrained from using the biologic characteristics of "accepted" paleoseeps, since many of them will be tested against the model later, however the usefulness of a synthesis paper could not be left out. Campbell and Bottjer (1995) compiled an excellent study of the fossils found from a few dozen "accepted" cold seeps and hydrothermal vents. They discovered articulate brachiopods; particularly *Rhynochonellides* and *Terebratulides* dominated the chemosynthetic realm from the Devonian through the Cretaceous. In the late Cretaceous they were replaced by bivalves, particularly from five families, all of whom have extant chemosymbiotic descendants (*Vesicomyidae, Mytilidae, Solemyidae, Thyasiridae, and Lucinidae)*, with the latter two being the most dominant, although it has been argued there is extreme preservation bias in these settings, leaving the geologic record of the actual faunal community considerably lacking (Callender and Powell 1999).

Microbes play a major role in chemosynthesis, either living as endosymbionts or living on their own, fixing compounds for higher organisms or other microbes to live on. *Beggiatoa*, a fluffy, white to orange sulfide oxidizing bacterial mat has been visually documented from several modern seeps (e.g. Zhang et al. 2002; Aharon and Fu 2000; Sassen et al. 1998).

This part of the test is not as concerned with the composition of the seep biota as it is that the seep community is in contrast with the surrounding background community. This is commonly referred to as an "oasis" setting where the area under study has a considerably higher density of organisms than does the surrounding community (Callender and Powell 1999).

Spatial Relationship to a Conduit for Fluid Flow

Methane conduits can prove difficult to identify. Often it is a sub-linear orientation of seep features resembling fault orientation at depth that leads an investigator to decide a deep seated fault lineament is responsible for fluid migration (Deyhle and Kopf 2001; Hovland 1992; Kauffman et al. 1996). Diffuse seepage is often attributed to accretionary prism dewatering (e.g. von Rad et al. 1996). Once again the actual mechanics of the conduit are not as important as demonstrating the presence of an available pathway for fluid migration, whatever form it may take. Since faults are the most common conduit called upon in both the modern and ancient, careful consideration of timing of faults is in order to assure a correct correlation. (c.f. Beauchamp and Savard 1992; Peckmann et al. 1999)

Organic Rich Source

Two types of methane exist with differing isotopic signatures resulting from different creation pathways. There are biogenic and thermogenic methane, each named for their style of generation. Bacterial consumption of organic matter and thermal degradation of organic matter are the two systems responsible (Cavagna et al. 1999). Thermogenic methane can have $\delta^{13}C$ values $-35^{0}/_{00}$ to $-50^{0}/_{00}$ while biogenic methane ranges from $-50^{0}/_{00}$ to $-80^{0}/_{00}$ (Claypool and Kaplan 1974; Zhang et al. 2002).

Absolute kinetic parameters dictate that thermogenic methane cannot be produced below 60°C (Snowdon et al. 1999), while the vast majority of thermogenic methane is produced at temperatures between 375 °C and 525 °C (Schaefer et al. 1999).

Methane can get trapped as gas hydrates in the lattice system of water ice typically in areas of low temperature, i.e. permafrost (>150m depth), or on the slope and rise of continental margins (water depth >300m) (Kvenvolden 1998). Many authors have pointed out this reservoir of carbon is likely much larger than the combined ocean-atmosphere carbon pools (e.g. Kennedy et al. 2001; Zhang et al. 2002), making it an intriguing alternative carbon reservoir.

Increasing temperature or decreasing pressure can release this methane since only the lattice of water ice need be broken. This suggests the terrestrial hydrates would be more likely to play an active role in the combined ocean-atmosphere system since there is a balancing effect of increasing temperature and increasing pressure which tends to keep the marine hydrates sequestered (Kvenvolden 1998). Although this would suggest marine hydrates have little chance of freedom, Hovland (1992) shows these hydrates are released in relation to ice berg scour marks on the sea floor demonstrating they are not deeply buried. This shallow burial leads to the possibility of hydrate bound methane being released during turbidity events on continental margins. There is however another possibility for this methane. Hydrate bound methane can be oxidized by microbes in situ (Zhang et al. 2002; Sassen et al.1998). As we will see in a moment, this has important implications for both the reactive methane pool as well as the chemically charged fluids released through this process.

Isotopically Light Stable Carbon Record

Most ancient cold seeps have been recognized via the isotopically light stable carbon recorded in the carbonates they produce (e.g. Campbell, 1992; Beauchamp and Savard, 1992; Peckmann et al. 2001), and these $\delta^{13}C$ depleted carbonates are also found in the modern (e.g. Paull et al. 1992; Deyhle and Kopf, 2001; Zhang et al. 2002; Elvert et al. 2000). Although there are various metabolic pathways capable of inducing carbonate precipitation, the presence of isotopically light carbonates is indicative of anaerobic methane oxidation forcing precipitation (Zhang et al. 2002; Sassen et al. 1998; Paull et al. 1992; Cavagna et al. 1999; Jahnke et al. 1999; Elvert et al. 2000).

There are many processes either directly or indirectly associated with the precipitation of carbonates, and I will discuss them in two "tiers". The first tier is the most indicative and best suited, and includes: Aerobic Oxidation of Methane (OM), Anaerobic Oxidation of Methane (AOM), Anaerobic Sulfate Reduction (ASR) and Aerobic Sulfide Oxidation (SO). A second tier of possible processes includes: Aerobic Organic Matter Decomposition (OD), Anaerobic Organic Matter Decomposition (AOD) [fermentative organic matter decomposition], and Anaerobic Sulfate Reduction of Organic Matter (ASRO).

Tier 1

Aerobic Oxidation of Methane (OM)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2\,H_2O \qquad \text{(eq. 1)}$$

Although this would produce depleted CO_2, it would also serve to increase acidity, making eq. 1 unlikely as the driver of carbonate precipitation (Jahnke et al. 1999; Paull et al. 1992; Cavagna et al. 1999).

Anaerobic Oxidation of Methane (AOM)

$$CH_4 + 2\,H_2O \rightarrow CO_2 + 4H_2 \qquad \text{(eq. 2a)}$$

or

$$2CH_4 + 2\,H_2O \rightarrow CH_3COOH + 4H_2 \qquad \text{(eq2b)}$$

This process usually occurs in conjunction with sulfate reduction, but can occur on its own (Orphan et al. 2001; Hinrichs et al. 2000). The sulfate reducers utilize the H_2 and the acetic acid produced in eq. 2b (Boetius et al. 2000; Orphan et al. 2001; Elvert et al. 2000; Valentine and Reeburgh 2000). Equation 2b is likely the dominant pathway in this coupled process as shown by the greater amount of energy it provides to each syntrophic partner, and the fact that methanogens have not been shown to be able to produce hydrogen in the presence of methane (Valentine et al. 2000). Eq. 2b also explains the presence of isotopically light biomarkers present in some sulfate reducers via direct carbon exchange with the methane oxidizers (Valentine and Reeburgh 2000)

Anaerobic Sulfate Reduction (ASR)

$$H^+ + 4H_2 + SO_4^{-2} \rightarrow HS^- + 4H_2O \qquad \text{(eq. 3a)}$$

and

$$CH_3COO + SO_4^{-2} \rightarrow 2HCO_3^- + HS^- \qquad \text{(eq. 3b)}$$

It is the combination AOM and ASR that are the dominant force behind carbonate precipitation (e.g. Zhang et al. 2002; Boetius et al. 2000, Cavagna 1999).When you combine eq. 2b with 3a and 3b you get the common representation of the coupling of anaerobic methane oxidation and sulfate reduction.

Coupled Anaerobic Methane Oxidation and Anaerobic Sulfate Reduction (CAMS)

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^- + HS^- + H_2O \qquad \text{(eq. 4)}$$

Until recently the presence of the consortium of microbes responsible for eq. 4 had only been inferred as a result of the sudden drop in SO_4^{-2} and increase in methane oxidation that occurs at the base of the sulfate reduction zone (e.g. Cavagna 1999) however some of these organisms have recently been positively identified. The microbes are bacteria (sulfate reducers) belonging to the *Desulfosarcinales/Desulfococcus* (DSS) group, or archea (methane oxidizers) belonging to the *Methanosarcinales* (ANME-2) group (Orphan et al. 2001; Valentine and Reeburgh 2000). The consortium (ANME-2/DSS) is composed of these individuals packed together in quasi-spherical arrangements with the sulfate reducers on the outside (Orphan et al. 2001; Boetius et al. 2000).

This coupled process can take place either as two distinct processes where individual, free living archea fix compounds for use by individual, free living bacteria, or in one process within the consortium ANME-2/DSS (Elvert et al. 2000; Orphan et al. 2001). The oxidation of methane alone is associated with isotopic fractionation, as is the reduction of sulfate alone. The $\delta^{13}C$ of the archea alone are lighter than the coexisting methane while the $\delta^{13}C$ of the bacteria are heavier than the surrounding methane (Orphan et al. 2001). This balance helps validates the argument made by many workers that CAMS provides bicarbonates that isotopically resemble the parent methane. It has been argued by some researchers that AOM was carried out by specialized archea (methanogens) who could consume methane instead of oxidizing it via "reverse methanogenesis", however the unlikelyhood of eq. 2a, which is "reverse methanogenesis", makes this possibility less attractive (see Valentine et al. 2000 and Valentine and Reeburgh 2000 for a full review).

Aerobic Sulfide Oxidation (SO)

$$HS^- + 2O_2 \rightarrow SO_4^{-2} + H^+ \qquad \text{(eq. 5)}$$

The delivery of HS^- into the oxygenated zone via eq. 4 provides a nutrient source for the sulfide oxidizers, mainly *Beggiatoa,* that are commonly found at the sediment/water interface of cold seeps (Cavagna et al. 1999; Boetius et al. 2000; Sassen et al. 1998; Zhang et al. 2002; von Rad et al. 1996; Aharon and Fu 2000).

Tier 2

Aerobic Organic Matter Decomposition (OD)

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad \text{(eq. 6)}$$

Although this produces depleted CO_2, it would also serve to increase acidity similar to eq. 1, suggesting this process alone is not responsible for carbonate precipitation (e.g. Paull et al. 1992).

Anaerobic Organic Matter Decomposition (AOD)

$$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2 \qquad \text{(eq. 7a)}$$

with

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\,H_2O \qquad \text{(eq. 7b)}$$

Notice the hydration in eq. 7b of only one CO_2 produced by eq. 7a, leaving the other out of the process. This is reflected in the typical shorthand of this equation.

$$2CH_2O \rightarrow CO_2 + CH_4 \qquad \text{(eq. 8)}$$

$H^{12}CO_3^-$ is preferentially used in eq. 8, being consumed ~7% faster than $H^{13}CO_3^-$, driving the CH_4 to lighter values, and consequently the residual CO_2 to heavier values (Mazzullo 2000; Teal et al. 2000). The heavy values of CO_2 produced in this manner have recently been used to explain anomalously heavy values (as high as $+17^0/_{00}$) found in some cold seep/seep suspect carbonates (Mazzullo 2000; Wu and Chafetz 2000; Teal et al. 2000), however this process is still under considerable debate. As with eq. 1, the simple introduction of CO_2 into the water column does not guarantee carbonate precipitation, and if anything would presumably lead to carbonate dissolution through increased acidity. Unless a source of increased alkalinity can be identified for an outcrop in question, this process is still highly suspect. How else can one explain the extreme $\delta^{13}C$ enrichment found in some carbonates?

Two interesting possibilities have recently arisen that fulfill this requirement. Tsunogai et al. (2000) report a change in $\delta^{13}C$ of methane with respect to flux. As the flux decreases, the $\delta^{13}C$ increases. AOM removes $^{12}CH_4$ preferentially leaving behind heavy residual methane, and by the time this methane gets near the surface, the $\delta^{13}C$ is considerably higher than the original methane, and can even reach positive values.

The other possibility is, in effect, *in situ* Rayleigh distillation of hydrate bound methane. Sassen et al. (1998) report a divergence between vent gas $\delta^{13}C$ and the residual hydrate bound methane $\delta^{13}C$. Over time this process would leave a reactive hydrate bound methane pool considerably enriched in $\delta^{13}C$. If this methane is later the source of a cold seep, the heavy parent methane would produce carbonates of similar enriched values.

Anaerobic Sulfate Reduction of Organic Matter (ASRO)

$$2CH_2O + SO_4^{-2} \rightarrow 2HCO_3^- + H_2S \qquad \text{(eq. 9)}$$

The bicarbonate produced in this manner would have an isotopic value of -21$^0/_{00}$ to -22$^0/_{00}$ (Joachimski and Buggisch 2000) reflecting the $\delta^{13}C$ of organic matter. Paull et al. (1992) suggest eq. 9 in conjunction with eq. 6 (OD) would provide an increase in isotopically light bicarbonate and reduce alkalinity stimulating precipitation. If this was the case, the bicarbonate responsible would come from eq. 9, producing a carbonate with a depleted $\delta^{13}C$ value of typical organic matter. Paull et al. (1992) also show an increase in the $\delta^{13}C$ of pore water Σ CO_2 with decreasing Σ CO_2 concentrations. This may be a concomitant effect of the process described by Tsunogai et al. (2000).

Summary of Isotopic Requirements

If the $\delta^{13}C$ values of carbonates studied through this diagnostic test yield abnormally depleted values (< -20$^0/_{00}$), there are few ways if any to accomplish this other than an extremely light carbon source such as methane. Extremely depleted values (<-40$^0/_{00}$) are not uncommon, and are the best indicator of the presence of methane.

The issue of abnormally heavy values (> +7$^0/_{00}$), is a much more complicated issue that is still awaiting resolution. These extreme examples of $\delta^{13}C$ enrichment demonstrate how much we have still to learn of the fundamental biogeochemical pathways affecting the overall ocean-atmosphere carbon cycle.

The -20$^0/_{00}$ to +7$^0/_{00}$ range chosen for significance is somewhat arbitrary, however the presence of geographically wide spread carbonates showing a global signal within the excluded range (-7$^0/_{00}$ < $\delta^{13}C$ < +7$^0/_{00}$) (c.f. Goddéris et al. 2001; Mii et al. 1999; Dao-Yi and Zheng 1993) suggests these values can be generated without the presence of methane. -20 $^{0}/_{00}$ was chosen as the lower limit due to the values produced through ASRO. Consequently, we must look for values of extreme depletion or enrichment.

Summary of General Requirements

(1)The metabolic pathways of chemosynthetic organisms, primarily CAMS, provides bicarbonate and increased alkalinity allowing precipitation of carbonates in unlikely settings. (2) Methane charged fluids escaping at the sediment/water interface will leave a physical record of their presence, usually a topographic feature such as a carbonate mound, chimney or mud volcano. (3) Methane provides an alternative energy source utilized by an exotic faunal assemblage in striking contrast to the surrounding non-seep fauna. (4) Structural features such as faults are most often the pathway for methane charged fluids to move. (5) An underlying organic rich unit is most often the source, but gas hydrates and deltaic complexes have both been shown to provide methane. (6) Extreme carbonate isotopic depletion in $\delta^{13}C$ is absolutely indicative of the presence methane. Consequently, this test is centered on recognition of the products of the oxidation of methane. Extreme carbonate $\delta^{13}C$ enrichment, although much less understood, is assumed to be a by-product of methanogenesis.

Application of Diagnostic Test

The preceding diagnostic test was developed upon modern examples of the biology, lithology, geochemistry, and structure of cold seeps. The purpose of the test is to allow absolute confirmation of cold seeps in the fossil record. In the case an outcrop studied satisfies all six criteria in the test, it should be readily accepted as a cold seep. The strength of the test is its ability to highlight those outcrops that are able to tell us something we don't fully understand. For example, an outcrop that has the faunal assemblage and structural features of a cold seep, yet lacks the extreme isotopic depletion, must be operating through biologic conditions and metabolic pathways we are yet to fully elucidate. The diagnostic test is here applied to five fossil cold seeps already argued as such in the literature.

Tepee Buttes (Colorado, USA)

Kauffman et al. 1996

1. **Anomalous Carbonates:** Conical "tepee" shaped buttes stand up to 30 m tall, consisting of an inner core of limestone surrounded by the Pierre Shale.
2. **Physical Feature:** The buttes owe their morphology to the upward movement of fluids.
3. **Assemblage:** Dominated by mollusks and microfauna which are larger and make up a larger body mass than the surrounding fauna.
4. **Conduit:** Hundreds of individual buttes have been mapped, mostly parallel to Laramide structural trends in the Front Range, Wet Mountains, and Los Animas Arch.
5. **Source:** The authors concluded the underlying organic rich Niobara Formation was the source.
6. **Isotopes:** Carbonate cements average -41$^{0}/_{00}$, making it well within the limits for certainty.

All six criteria were met by this site, so there is little doubt it was the result of methane charged fluids migrating from depth and being oxidized anaerobically.

Harz Mountains (Germany)

Peckmann et al. 2001

1. **Anomalous Carbonates:** Although not referred to as such by the authors, there are none the less carbonates. This part of the test does not require the limestones be anomalous, just that there be limestone.
2. **Physical Feature:** None specifically mentioned by the authors as they were studying primarily the seep community.
3. **Assemblage:** Specifically referenced as high abundance – low diversity, the fauna is dominated by *Rhynochonellides* brachiopods with some *Solemyidae* bivalves.
4. **Conduit:** Again, the authors were primarily concerned with biology, but do mention neptunian dikes, without assigning them causality. Without detailed information of the nature of the relationship between the dikes and the carbonates, nothing may be concluded by this investigator relating to the conduit.
5. **Source:** The authors point out the source has never been positively identified, but a probable source unit, the Devonian Wissenbach Shale, is known to have been the source for migrating hydrocarbons in the region at the time of deposition. Furthermore, the presence of the mineral impsonite validates this as it is the result of the metamorphism of petroleum.
6. **Isotopes:** There is an interesting range of values present at this locality ($-7^{0}/_{00}$ to $-32^{0}/_{00}$). The extreme negative values are most likely the result of the oxidation of methane, yet the less negative values are intriguing.

The authors' focus on the biology leaves something to be desired for application of the test however the biologic community and the extreme isotopic depletion are both present and are the two most important indicators. This locality points out the need for the other features in the test. If the isotopic range were ($-7^0/_{00}$ to $-20^0/_{00}$) the conclusion there was methane present, or for that matter that it was being oxidized, would be much more spurious. The most important localities we can study are those which give us a wide range of values perhaps indicative of several metabolic zones being preserved essentially *in situ*. This fossilized living arrangement for the whole microbial community would be paramount in aiding our understanding of these processes.

SW Washington (USA)

Campbell 1992

1. **Anomalous Carbonates:** The proposed seep is in the Quinault formation, which consists of sandstones, siltstones and conglomerates. Authigenic carbonates are restricted to the suspect area.
2. **Physical Feature:** Although not expressly mentioned as the cause of the carbonates, the author points out the occurrence of underlying strata piercing the Quinault formation via mud volcanoes.
3. **Assemblage:** Mollusks dominate, including *Lucinoma* and *Solemya.* This assemblage is not found elsewhere within the Quinault Formation.
4. **Conduit:** Mud diapirs, shear zones, and faults are all possible causes given by the author, as all are present at the locality. As evidence the author points out a modern gas mound (Garfield gas mound) quite close to the locality is fed by a mud volcano.

5. **Source:** Accretionary prism dewatering is the most likely candidate for this convergent margin setting.
6. **Isotopes:** The range of values is -20$^0/_{00}$ to -35$^0/_{00}$, in good accordance with thermogenic methane as the carbon source.

This locality can also be accepted as a fossil cold seep since it has satisfied all six requirements. This is an excellent example of the isotopic values one would expect from a carbon source of thermogenic methane being created at depth as subduction takes place.

Sverdrup Basin (Canadian Arctic)

Beauchamp and Savard 1992

1. **Anomalous Carbonates:** The Christopher Formation consists of shale and siltstone including anomalous carbonate mounds.
2. **Physical Feature:** Carbonate mounds have long avoided explanation and methane has offered an attractive solution. Just as in a mud volcano, the overall geometry is a result of the upward movement of fluids from depth.
3. **Assemblage:** *Terebratulid* brachiopods, numerous bivalves, and tube worms make up the community, which is much denser and contains more biomass than the surrounding community.
4. **Conduit:** The authors describe two locations in this work, each with a unique conduit. In one locality a salt dome created radial faults, along which the carbonate mound is located. At the other site, the mound is located along a master listric fault from a half-graben.
5. **Source:** The Jurassic Ringnes Formation is the most likely source, as described by the authors.

6. **Isotopes:** The primary cements range from $-35^0/_{00}$ to $-50^0/_{00}$. This is in good accordance with biogenic methane as the carbon source. The lack of compressional tectonics suggests it was not thermogenic methane, as do the isotopes.

This is yet another example of a locality that should be accepted as a fossil cold seep. It has easily met each criterion, and is one of the more complete surveys in the literature.

Sacramento Mountains (USA)

Wu and Chafetz 2002

1. **Anomalous Carbonates:** Similar to the Harz Mountains, the entire sequence containing the locality consists of primarily carbonates.
2. **Physical Feature:** The presence of carbonate mounds in the Alamogordo Member of the Lake Valley Formation has long puzzled investigators.
3. **Assemblage:** The authors make no mention of biota, only referring to brachiopods in relation to $\delta^{13}C$ values measured from them.
4. **Conduit:** This is particularly troublesome. The authors cite neptunian dikes as the possible conduit, although there are some problems with this interpretation. First of all, not all mounds in their study have dikes associated with them suggesting there is no genetic link. They explain the dikes themselves as the result of differential loading from the high relief of the mound. If the mound already had high relief to cause the dike, the dike could not have created the mound. They conclude this argument by asserting the mounds grew, then the dikes formed, and then they served as conduits. How then, this investigator asks, did the mounds initiate?

5. **Source:** There is no mention of source. This is due to the fact the authors are invoking methanogenesis as the cause of precipitation. This essentially is then the source of methane.

6. **Isotopes:** The isotopes range from $+2^0/_{00}$ to $+5^0/_{00}$. This does not fall within the range of significance.

This outcrop is considerably different than the others discussed above, and highlights the test's requirement of methane oxidation for proper identification. The authors invoke methanogenesis as the carbon source as in eq. 7a and 7b, and that the carbonates produced are the sole result of the CO_2 exolved during methanogenesis. They make no further mention of the co-genetic methane, leaving one to assume it is not being oxidized and simply displaced into the ocean.

This investigator disagrees with their interpretation based upon several factors. (1) The formation of carbonates as a sole result of the CO_2 produced by methanogenesis (as described by Mazzullo 2000) results in predominantly dolomite mineralization. The carbonates measured by Wu and Chafetz (2000) are all low-Mg calcite microspar, not the dolomite described by Mazzullo. (2) The inability to reconcile the timing of the neptunian dikes; coupled with the fact other mounds in the study are not associated with dikes leaves the origin of the mounds shrouded in mystery. (3) The narrow range of carbon isotopic values at this locality ($+2^0/_{00}$ to $+5^0/_{00}$) is present in global signatures throughout the Mississippian (c.f. Mii et al. 1999). These values could simply be the result of asynchronous precipitation during one of the global isotopic events in the Carboniferous. Isotopic excursions are known to occur during significant disturbances in the global marine circulation system (c.f. Jeppsson 1990). (4) The lack of a record of the oxidation of methane, which seems to be ubiquitous in modern cold seeps is puzzling. This could be the result of sampling performed by the authors. The entire mound complex is considerably taller than their highest sample measured. The isotopic values reported could be the result of the shift in $\delta^{13}C$ that occurs with depth (fig. 3a and 3b). Perhaps the researchers only collected the lowermost region in this complex ecosystem.

It seems to this investigator there are other possible explanations worth a closer look. The $\delta^{13}C$ shift towards enriched values that occurs with decreasing methane flux (fig. 6) could account for the range of values seen at this site. If this were the case however, it follows there should be increasingly depleted $\delta^{13}C$ values down section as reported by Tsunogai et al. (2000). However, as the researchers point out, the base of the mounds are covered rendering this line of investigation difficult.

Another possibility is the removal of light methane through Rayleigh distillation in methane hydrates leaving behind hydrate-bound heavy methane; if this were later a source it could produce enriched values. The search for evidence of the initial expulsion of depleted methane becomes paramount to prove this argument.

Conclusion

This work is an attempt to more accurately define cold seeps in the rock record. Its application has highlighted the localities and fields of study requiring more research. The six criteria set out here offer a positive identification of four of the five tested fossil cold seeps, and adds insight to our lack of understanding of the fifth. With the amount of work being done on methane and chemosynthesis, this work can help researchers connect localities with similar scenarios to broaden our context of this bizarre ecosystem. Hopefully, more reports of carbonates with values such as those reported by Wu and

Chafetz (2002) will lead to some better understanding of this alternative process we are yet to properly define. The test contained herein is particularly useful for application to these anomalous settings since it gives us some direction towards reconciling them with the "normal" cold seep record. Further assistance may be provided by the addition of microbial sedimentary structures to the literature just now being developed and proposed (Noffke et al. 2001). It is through this effort of standardization we will find the truly anomalous, worthy of intensive study.

REFRENCES CITED

Aharon, P., and Fu, B., 2000, Microbial sulfate reduction rates and sulfur and oxygen isotope fractionations at oil and gas seeps in deepwater Gulf of Mexico: Geochimica et Cosmochimica Acta, v. 64, p. 233-246.

Ballard, R.D., 1977, Notes on a major oceanographic find: Oceanus (Woods Hole), v. 20, p. 35-44.

Beauchamp, B., and Savard, M., 1992, Cretaceous chemosynthetic carbonate mounds in the Canadian Arctic: Palaios, v. 7, p. 434-450.

Boetius, A., Ravenshlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gleseke, A., Amman, R., Jorgensen, B.B., Witte, U., and Pfannkuche, O., A marine microbial consortium apparently mediating anaerobic oxidation of methane: Nature, v. 407, p. 623-626.

Campbell, K.A., 1992, Recognition of a Mio-Pliocene cold seep setting from the Northeast Pacific convergent margin, Washington, U.S.A.: Palaios, v. 7, p. 422-433.

Campbell, K.A., and Bottjer, D.J., 1993, Fossil cold seeps: Research and Exploration, v. 9, p. 326-343.

Campbell, K.A., and Bottjer, D.J., 1995, Brachiopods and chemosymbiotic bivalves in Phanerozoic hydrothermal vent and cold seep environments: Geology (Boulder), v. 23, p. 321-324.

Callender, W.R., and Powell, E.N., 1999, Why did ancient chemosynthetic seep and vent assemblages occur in shallower water than they do today?: International Journal of Earth Sciences, v. 88, p. 377-391.

Cary, S.C., Fisher, C.R., and Felbeck, H., 1988, Mussel growth supported by methane as sole carbon and energy source: Science, v. 240, p. 78-80.

Cavagna, S., Clari, P., and Martire, L., 1999, The role of bacteria in the formation of cold seep carbonates: Geologic evidence from Monferrato (Tertiary, NW Italy): Sedimentary Geology, v. 126, p. 253-270.

Cavanaugh, C.M., Levering, P.R., Maki, J.S., Mitchell, R., and Lidstrom, M.E., 1987, Symbiosis of methylotrophic bacteria and deep sea mussels: Nature (London), v. 325, p. 346-348.

Claypool, G.E., and Kaplan, I.R., 1974, The origin and distribution of methane in marine sediments: Marine Science, v. 3, p. 99-139.

Corliss, J.B., Bainbridge, A., Ballard, R.D., Crane, K., Dymond, J., Edmond, J.M., Gordon, L.I., Green, K., Van Andel, T.H., Von Herzen, R.P., and Williams, D., 1979, Submarine thermal springs on the Galapagos Rift: Science, v. 203, p. 1073-1083.

Corselli, C., and Basso, D., 1996, First evidence of benthic communities based on chemosynthesis on the Napoli mud volcano (Eastern Mediterranean): Marine Geology, v. 132, p. 227-239.

Dao-Yi, X., and Zheng, Y., 1993, Carbon isotope iridium event markers near the Permian/Triassic boundary in the Meishan section, Zhejiang Province, China: Paleogeography, Paleoclimatology, Paleoecology, v. 104, p. 171-176.

Deyhle, A., and Kopf, A., 2001, Deep fluids and ancient pore waters at the backstop: Stable isotope systematics (B,C,O) of mud-volcano deposits on the Mediterranean Ridge accretionary system: Geology (Boulder), v. 29, p. 1031-1034.

Elvert, M., Suess, E., Greinert, J., and Whiticar, M.J., 2000, Archaea mediating anaerobic methane oxidation in deep-sea sediments at cold seeps of the eastern Aleutian subduction zone: Organic Geochemistry, v. 31, p. 1175-1187.

Goddéris, Y., François, L.M., and Veizer, J., 2001, The early Paleozoic carbon cycle: Earth and Planetary Science Letters, v. 190, p. 181-196.

Hinrichs, K.U., Summons, R.E., Orphan, V., Sylva, S.P., and Hayes, J.M., 2000, Molecular and isotopic analysis of anaerobic methane-oxidizing communities in marine sediments: Organic Geochemistry, v. 31, p. 1685-1701.

Hovland, M., 1992, Hydrocarbon seeps in northern marine waters – Their occurrence and effects: Palaios, v. 7, p. 376-382.

Jahnke, L.L., Summone, R.E., Hope, J.M., and Des Marais, D.J., 1999, Carbon isotopic fractionation in lipids from methanotrophic bacteria II: The effects of physiology and environmental parameters on the biosynthesis and isotopic signatures of biomarkers: Geochimica et Cosmochimica Acta, v. 63, p. 79-93.

Jeppsson, L., 1990, An oceanic model for lithological and faunal changes tested on the Silurian record: Journal of the Geological Society, London, v. 147, p. 663-674.

Joachimski, M.M., and Buggisch, W., 1999, Hydrothermal origin of Devonian conical mounds (kess-kess) of Hamar Lakhdad Ridge, Anti-Atlas, Morocco: Comment and Reply: Geology (Boulder), v. 27, p. 863-864.

Kauffman, E.G., Arthur, M.A., Howe, B., and Scholle, P.A., 1996, Widespread venting of methane-rich fluids in the Late Cretaceous (Campanian) submarine springs (Tepee Buttes), Western Interior seaway, U.S.A.: Geology (Boulder), v. 24, p. 799-802.

Kennedy, M.J., Christie-Blick, N., and Sohl, L.E., 2001, Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals?: Geology (Boulder), v. 29, p. 443-446.

Kulm, L.D., and Suess, E., 1990, Relationship between carbonate deposits and fluid venting – Oregon accretionary prism: Journal of Geophysical Research – Solid Earth and Planets, v. 95, p. 8899-8915.

Kvenvolden, K.A., 1998, A primer on the geological occurrence of gas hydrates, *in* Henriet, J.P., and Meienert, J., (eds), Gas hydrates: Relevance to world margin stability and climate change: Geological Society (London) Special Publication, v. 137, p. 9-30.

MacAvoy, S.E., Macko, S.A., and Joye, S.B., 2002, Fatty acid carbon isotope signatures in chemosynthetic mussels and tube worms from the Gulf of Mexico hydrocarbon seep communities: Chemical Geology, v. 185, p. 1-8.

Mazzullo, S.J., 2000, Organogenic dolomitization in peritidal to deep-sea sediments: Journal of Sedimentary Research, v. 70, p. 10-23.

Mii, H.S., Grossman, E.L., and Yancey, T.E., 1999, Carboniferous isotope stratigraphies of North America: Implications for Carboniferous paleoceanography and Mississippian Glaciation: Geological Society of America Bulletin, v. 111, p. 960-973.

Noffke, N., Gerdes, G., Klenke, T., and Krumbein, W.E., 2001, Microbially induced sedimentary structures – A new category within the classification of primary sedimentary structures: Journal of Sedimentary Research, v. 71, p. 649-656.

Orange, D.L., Greene, H.G., Reed, D., Martin, J.B., McHugh, C.M., Ryan, W.B.F., Maher, N., Stakes, D., and Barry, J., 1999, Widespread fluid expulsion on a translational continental margin: Mud volcanoes, fault zones, headless canyons, and organic-rich substrate in Monterey Bay, California: Geological Society of America Bulletin, v. 111, p. 992-1009.

Orphan, V.J., House, C.H., Hinrichs, K.U., McKeegan, K.D., and DeLong, E.F., 2001, Methane-consuming archaea revealed by directly coupled isotopic and phylogenetic analysis: Science, v. 293, p. 484-487.

Pancost, R.D., Hopmans, E.C., Sinninghe Damsté, J.S., and the MEDINAUT Shipboard Scientific Party, 2001, Achaeal lipids in Mediterranean cold seeps: Molecular proxies for anaerobic methane oxidation: Geochimica et Cosmochimica Acta, v. 65, p. 1611-1627.

Paull, C.K., Chanton, J.P., Neumann, A.C., Coston, J.A., and Martens, C.S., 1992, Indicators of methane-derived carbonates and chemosynthetic organic carbon deposits: Examples from the Florida Escarpment: Palaios, v. 7, p. 361-375.

Peckmann, J., Walliser, O.H., Riegel, W., and Reitner, J., 1999, Signatures of hydrocarbon venting in Middle Devonian carbonate mound (Hollard Mound) at the Hamar Laghad (Antiatlas, Morocco): Facies, v. 40, p. 281-296.

Peckmann, J., Gischler, E., Oschmann, W., and Reitner, J., 2001, An Early Carboniferous seep community and hydrocarbon-derived carbonates from the Harz Mountains, Germany: Geology (Boulder), v. 29, p. 271-274.

Rio, M., Roux, M., Renard, M., and Schein, E., 1992 Chemical and isotopic features of present day bivalve shells from hydrothermal vents or cold seeps: Palaios, v. 7, p. 351-360.

Sassen, R., MacDonald, I.R., Guinasso, N.L. Jr., Joye, S., Requejo, A.G., Sweet, S.T., Alcalá-Herrera, J., DeFreitas, D.A., and Schink, D.R., 1998, Bacterial methane oxidation in sea-floor gas hydrate: Significance to life in extreme environments: Geology (Boulder), v. 26, p. 851-854.

Schaefer, R.G., Galushkin, Y.I., Kolloff, A., and Littke, R., 1999, Reaction kinetics of gas generation in selected source rocks of the West Siberian Basin: Implications for the mass balance of early-thermogenic methane: Chemical Geology, v. 156, p. 41-65.

Snowdon, L.R., Collett, T.S., (ed), and Uchida, T., (ed), 1999, Methane and carbon dioxide gas-generation kinetics, JAPEX/JNOC/GSC Malik 2L-38 gas hydrate research well: Bulletin – Geological Survey of Canada, v. 544, p. 125-141.

Teal, C., Mazzullo, S.J., and Bischoff, W.D., 2000, Dolomitization of Holocene shallow-marine deposits mediated by sulfate reduction and methanogenesis in normal-salinity seawater, Northern Belize: Journal of Sedimentary Research, v. 70, p. 649-663.

Tsunogai, U., Yoshida, N., Ishibahi, J., and Gamo, T., 2000, Carbon isotopic distribution of methane in deep-sea hydrothermal plume, Myojin Knoll Caldera, Izu-Bonin arc: Implications for microbial methane oxidation in the oceans and application to heat flux estimation: Geochimica et Cosmochimica Acta, v. 64, p. 2439-2452.

Tunnicliffe, V., 1992, The nature and origin of the modern hydrothermal vent fauna: Palaios, v. 7, p. 338-350.

Valentine, D.L., and Reeburgh, W.S., 2000, New perspectives on anaerobic methane oxidation: Environmental Microbiology, v. 2, p. 477-484.

Valentine, D.L., Blanton, D.C., and Reeburgh, W.S., 2000, Hydrogen production by methanogens under low-hydrogen conditions: Archives of Microbiology, v. 174, p. 415-421.

von Rad, U., Rösch, H., Berner, U., Geyh, M., Marchig, V., and Schulz, H., 1996, Authigenic carbonates derived from oxidized methane vented from the Makran accretionary prism off Pakistan: Marine Geology, v. 136, p. 55-77.

Wiedicke, M., Neben, S., and Spiess, V., 2001, Mud volcanoes at the front of the Makran accretionary complex, Pakistan: Marine Geology, v. 172, p. 57-73.

Wu, Y., and Chafetz, H.S., 2002, ^{13}C-Enriched carbonate in Mississippian mud mounds: Alamogordo Member, Lake Valley Formation, Sacramento Mountains, New Mexico, U.S.A.: Journal of Sedimentary Research, v. 72, p. 138-145.

Zhang, C.L., Li, Y., Wall, J.D., Larsen, L., Sassen, R., Huang, Y., Wang, Y., Peacock, A., White, D.C., Horita, J., and Cole, D.R., 2002, Lipid and carbon isotopic evidence of methane-oxidizing and sulfate-reducing bacteria in association with gas hydrates from the Gulf of Mexico: Geology (Boulder), v. 30, p. 239-242.

FIGURE CAPTIONS

Figure 1. Chart showing the change in dominant preserved fauna over time (from Campbell and Bottjer1995).

Figure 2a. Example of structurally focused fluid expulsion from the Mediterranean (from Deyhle and Kopf 2001).

Figure 2b. Sketch of the physiographic features created by seeping fluids in Monterey Bay (from Orange et al. 1999)

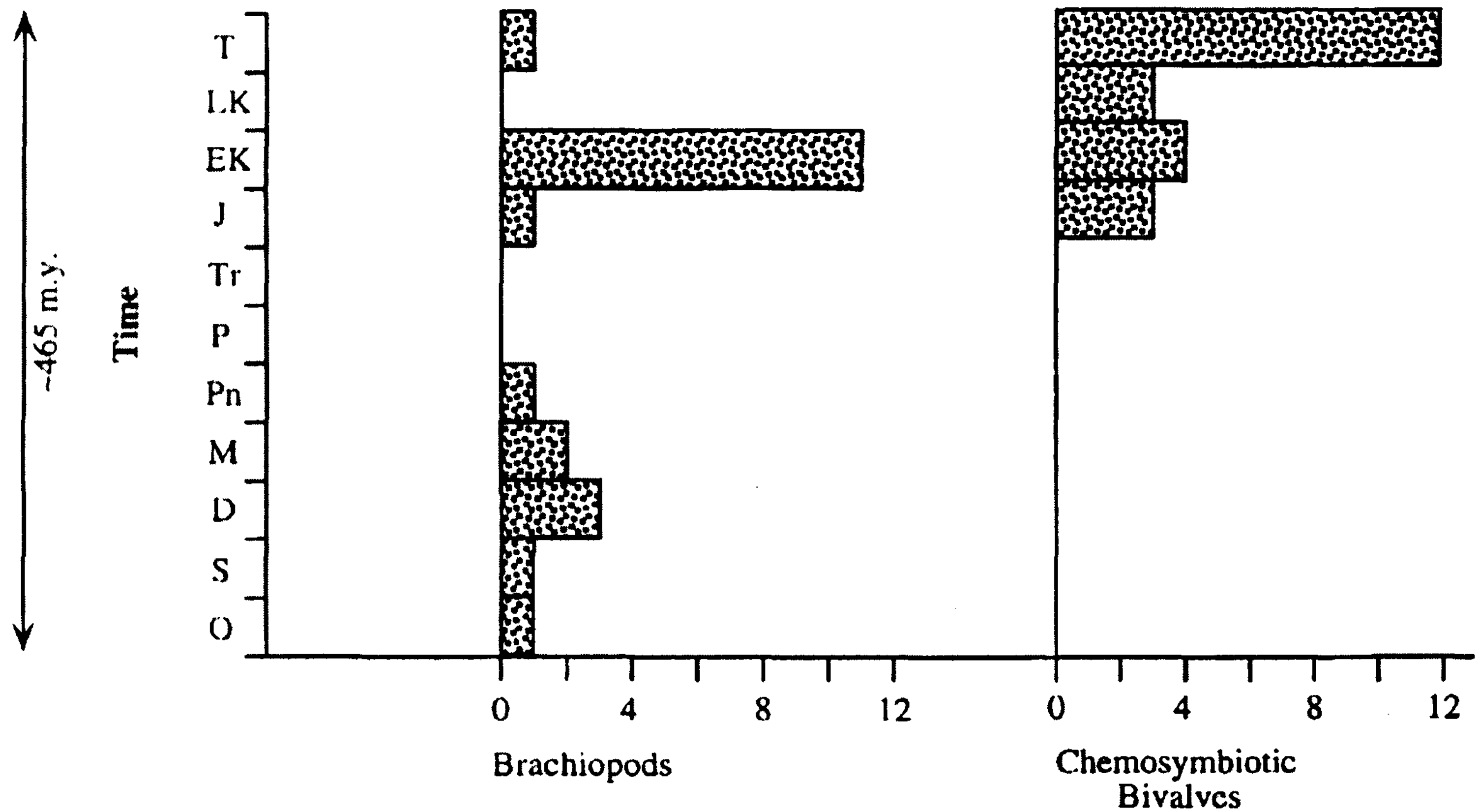
Figure 3a. Change in $\delta^{13}C$ occurring with depth, notice positive increase as you move down section (from Mazzullo 2000).

Figure 3b. Change in $\delta^{13}C$ with depth, notice the positive increase as in fig. 3a, but this time the shift does not result in positive values (from Tsunogai et al. 2000).

Figure 4. Diagram of the major metabolic pathways occurring in a cold seep setting (from Cavagna et al. 1999).

Figure 5. Sketch of the ANME-2/DSS consortium and the change in $\delta^{13}C$ as you move through the organism (from Orphan et al. 2001).

Figure 6. Plot of $\delta^{13}C$ versus methane flux. The decrease in flux results in a positive $\delta^{13}C$ shift even to positive values (from Tsunogai et al. 2000)



Number of Appearances in Hydrothermal Vents and Cold Seeps

Figure 1: Cramer 2002

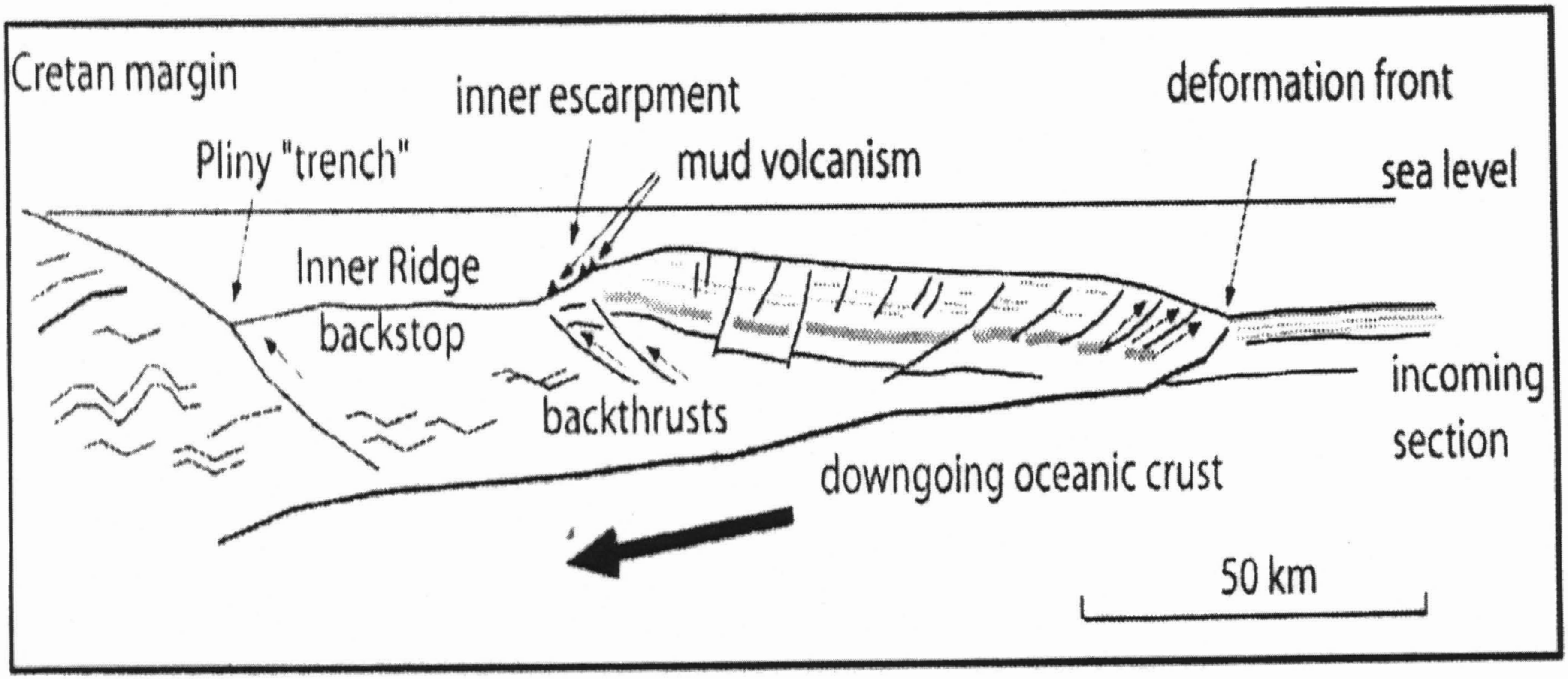


Figure 2a: Cramer 2002

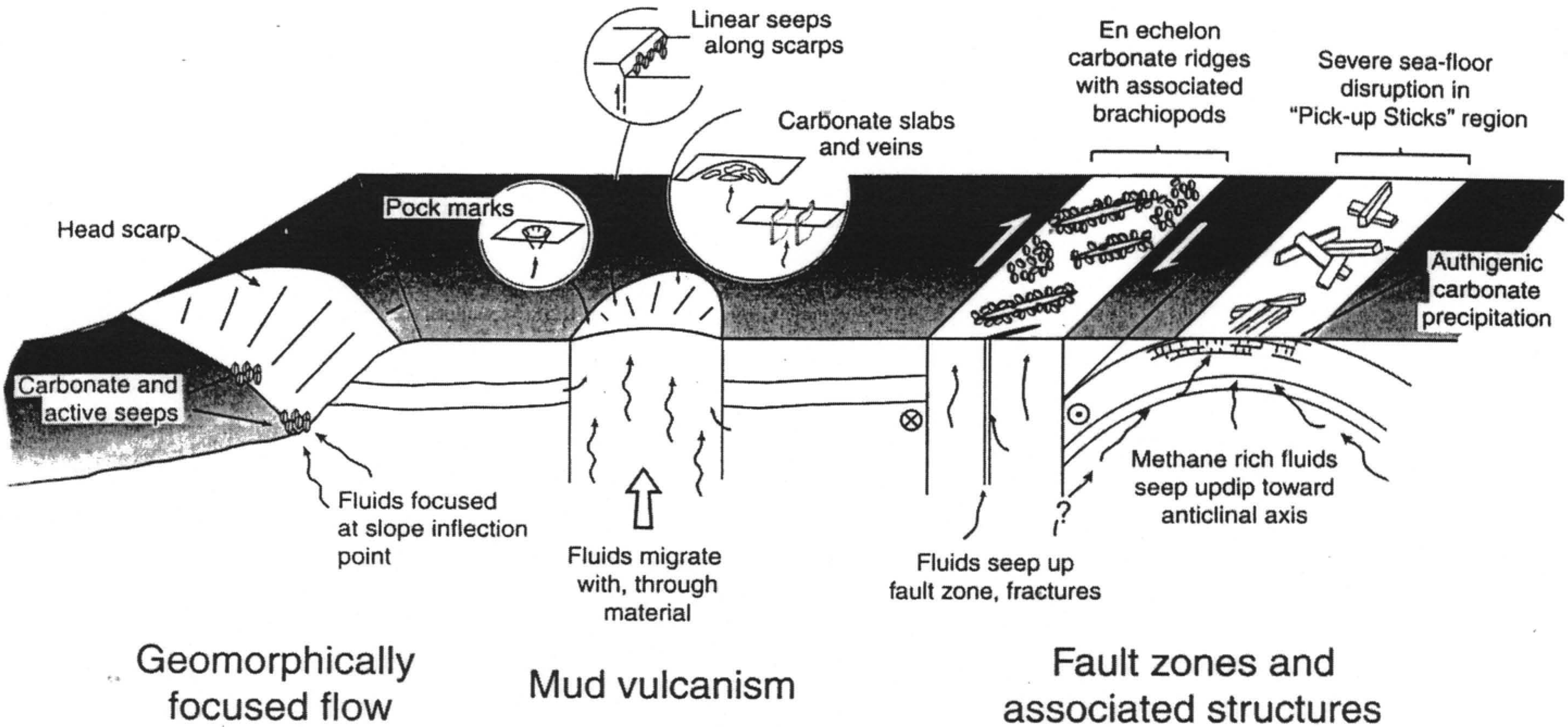


Figure 2b: Cramer 2002

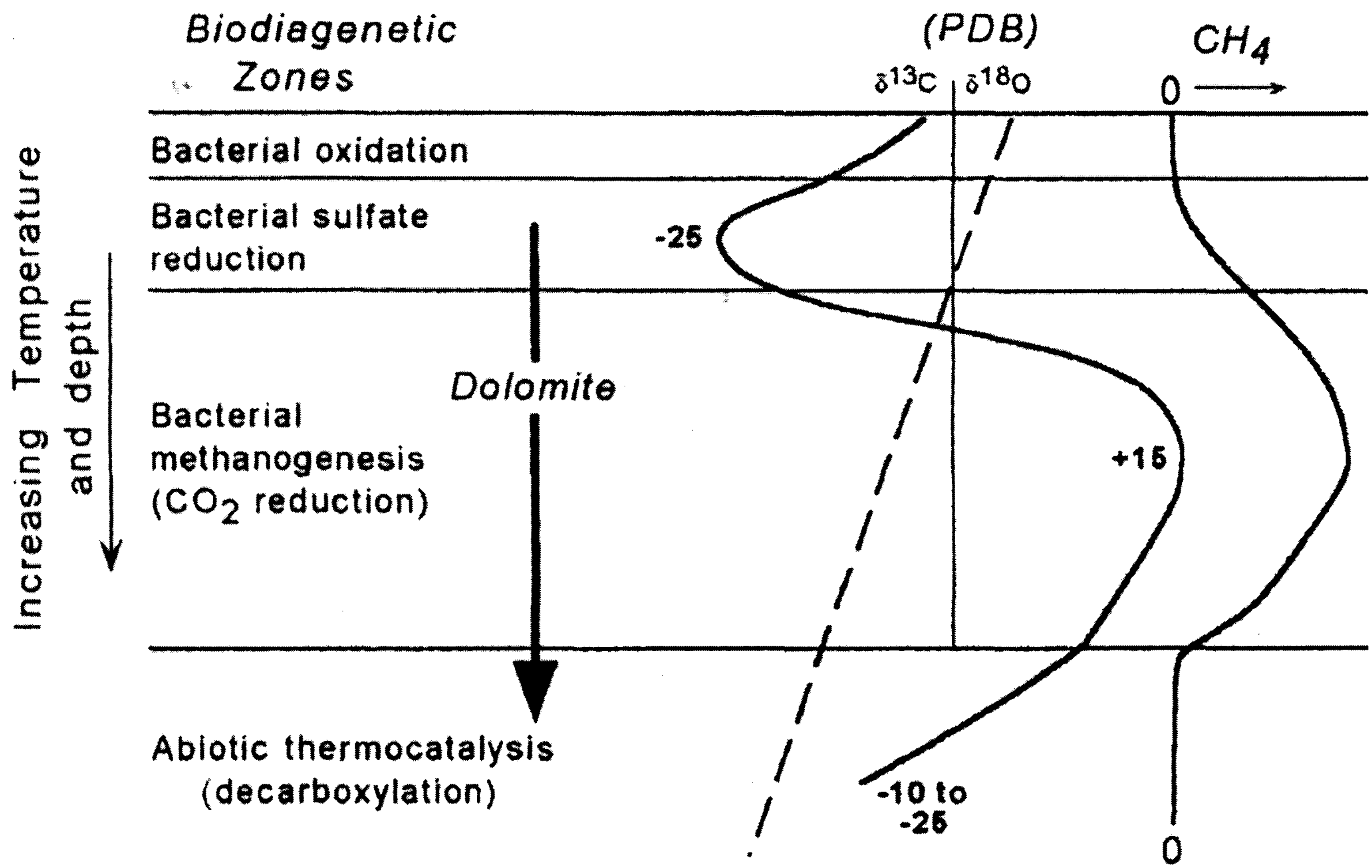


Figure 3a: Cramer 2002

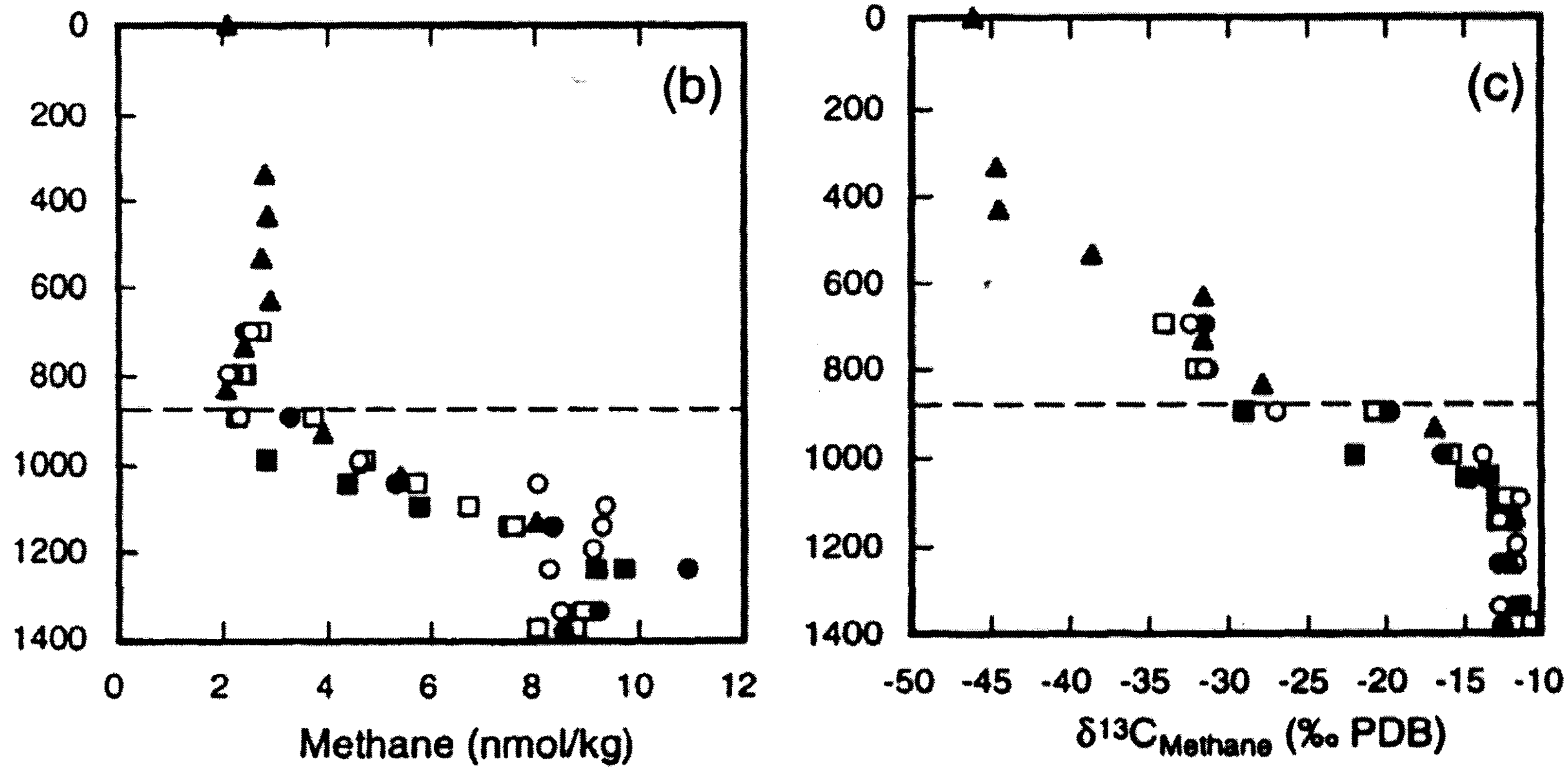


Figure 3b: Cramer 2002

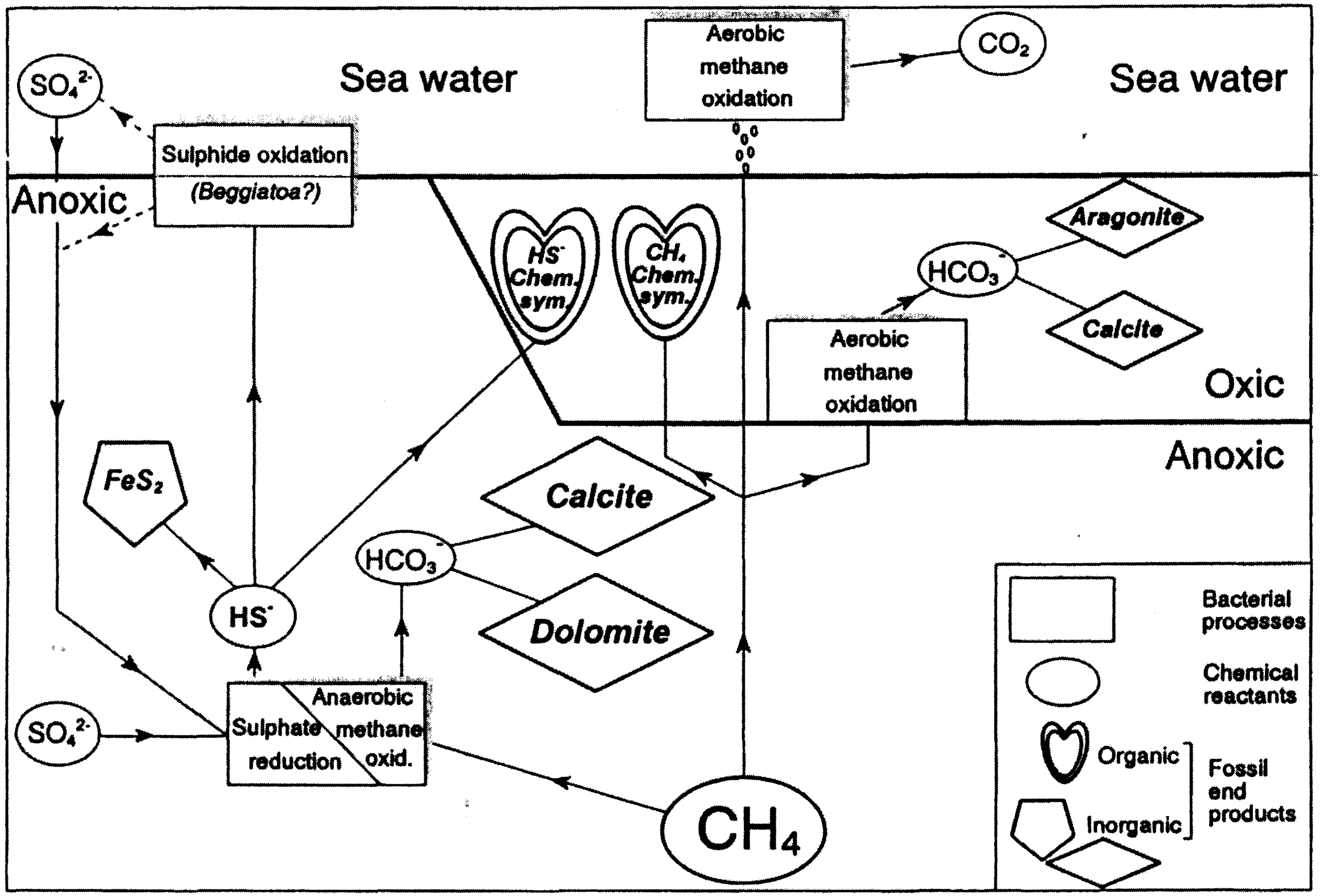


Figure 4: Cramer 2002

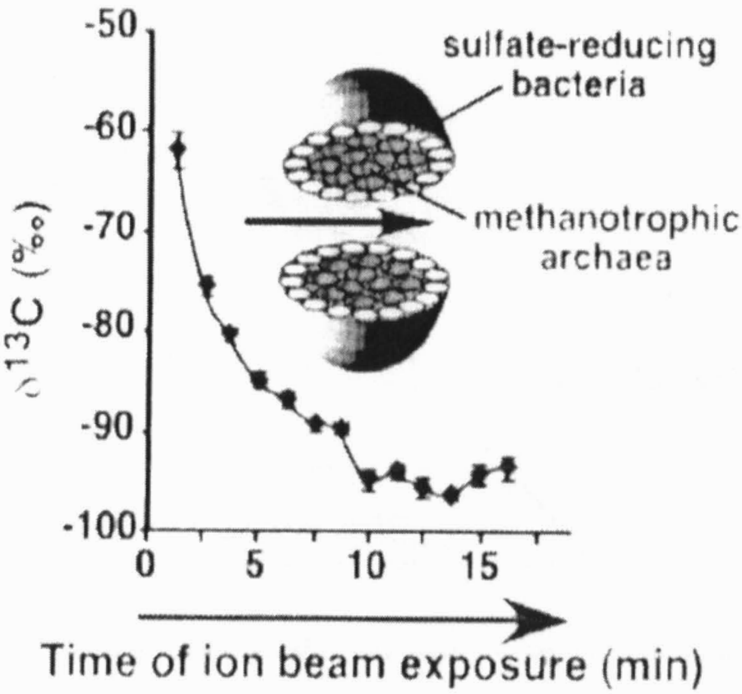


Figure 5: Cramer 2002

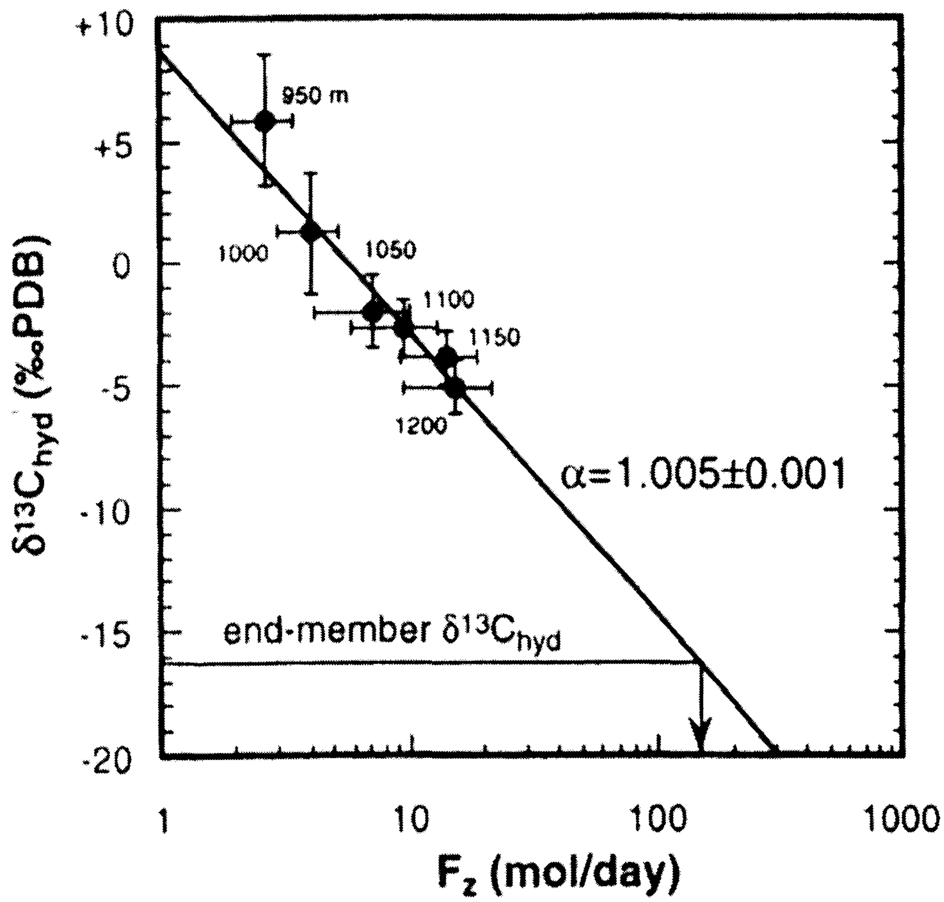


Figure 6: Cramer 2002